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MICROWAVE OVEN IN SYNTHESIS OF Na-ZEOLITES FROM FLY ASH (PRELIMINARY RESULTS)

Abstract. Fly ash — the finest fraction of coal combustion wastes — can be transformed into zeolites because of its high content of Si and Al. Samples of fly ash collected from power plants in Kraków were activated using NaOH and NaCl solutions of various concentrations in microwave ovens of two types. Sodalite, hydroxysodalite, NaP1 (gismondine type), and analcime were obtained in syntheses under various conditions. The highest zeolite productivity was observed during reactions with a presence of Cl anions (beside OH groups) in activation solution. Application of the microwave oven shortens the time of synthesis to minutes, but results of reactions are more difficult to predict than those in hydrothermal synthesis.

Key-words: fly ash, zeolite synthesis, microwave oven, salt effect

INTRODUCTION

Problems of deposition and utilization of coal combustion wastes become more serious every year. Fly ash is trapped on filters in chimneys of power plants, then deposited in reservoirs and on dumps. From there it can be transported and dispersed by winds, polluting soil and water. Negative impact on local ecosystems has already been noticed (Tyson 1997).

Mineral composition of fly ash depends on the content and composition of mineral matter in coal. The main components are aluminosilicate glass, mullite and quartz; residuum of coal matter is subordinate, while carbonates, Fe-oxides, sulphates, feldspars, tridymite and cristoballite are present rarely (Querol et al. 1995; Amrhein et al. 1996; Wilczyńska-Michalik, Michalik 1996; Chang, Shih 1998).

The finest ash wastes (Si, Al, Ca, Fe, Na, K, subordinate Mg, Ti, Mn, Zn, Cu, Pb and C, S, P, N) show a high content of deleterious elements. Heavy metals can be eluted by meteoric water from fly ash because of their weak bounding in aluminosilicate glass (Bahranowski et al. 1999). So, in spite of the presence of beneficial nutrients, fly ash is rarely applied in soil fertilization (Amrhein et al. 1996). However, it is widely used as

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a component in materials for building industry, in mining (i.e. as backfill) and can also be utilized as a cheap sorbent of water pollutants (Hari Babu et al. 1993).

The composition of fly ash renders it transformable into zeolites and related aluminosilicates as its significant content of aluminosilicate glass and mullite stimulates easy conversion during treating by alkaline hydroxide solutions. Laboratory hydrothermal synthesis of low-Si zeolites is similar to processes of basaltic glass transformation occurring in nature (Wirsching 1981; Kawano, Tomita 1997; Hall 1998; Christidis et al. 1999). Research on the synthesis of zeolite phases from post-incineration wastes was carried out in many countries (Berkgaut, Singer 1996; Querol et al. 1997b; Yang, Yang 1998; Ma et al. 1998; Hollman et al. 1999) and also successfully in Poland (Sarbak, Kramer-Wachowiak 1997, 1998; Michalik, Wilczyńska-Michalik 1998). Various zeolite phases were obtained during hydrothermal transformation of fly ash: NaP1, sodalite, faujasite, analcime, nepheline hydrate, hydroxycancrinite, phillipsite, F Linde, and others (nomenclature and classification of zeolite phases after Querol et al. 1997a, Baerlocher et al. 2001 and Treacy, Higgins 2001). Fly ash was activated in Na or K hydroxide solution, also with addition of chlorides, for few hours to few months, in the temperature range 60–550°C

A microwave oven is a modern and effective device in zeolite synthesis as it shortens reactions to minutes (Querol et al. 1997a). Thus, it seems to be a very promising equipment for further research on synthesis or modification of zeolites (Park, Komarneni 1998).

Fly ash from power plants localized in Kraków was examined in the past as a potential substrate for zeolite synthesis. Several zeolite phases were obtained during different hydrothermal syntheses: sodalite and hydroxysodalite, NaP1, faujasite and chabasite, in the time varying from ten hours to seven days (Derkowski 2001, and unpublished data). The possibilities of transformation of fly ash from the power plants of the Kraków area into zeolite materials were proved. Microwave oven processing could effectively shorten reactions or show a new way of such a synthesis of zeolites. Positive results of further research can bring new outlook at utilization of fly ash.

MATERIALS AND METHODS

The samples of fly ash were collected from power plants in Kraków: Huta im. T. Sendzimira (T. Sendzimir Steelworks — samples H) and Elektrociepłownia Kraków S.A. — ECK (Kraków Power/Heating Plant — samples E).

Materials

Fresh samples (both H and E) show very similar mineral composition: mullite and quartz (in various ratio), unburned coal matter, occasionally gypsum, calcite, feldspars (Fig. 1). The content of aluminosilicate glass is difficult to evaluate. Chemical composition of fly ash from the ECK power plant (Table 1) was determined in Ancaster

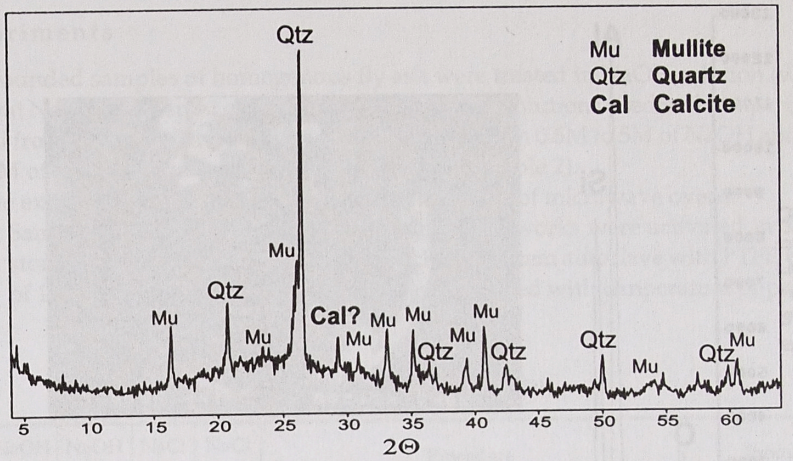

Fig. 1. XRD pattern of fly ash from T. Sendzimir Steelworks

Laboratories, Canada, *via* GEOANALIZA, Kraków. The SiO_2/Al_2O_3 wt. ratio of fly ash from the ECK power plant is approximately 1.878 (Si/Al atomic ratio ≈ 1.594).

In SEM observations glass occurs as spherical forms with rough and smooth surfaces (Fig. 2). Elements of electrostatic precipitators from a power plant were found as elongated particles of metallic iron or iron oxides (Fig. 3).

TABLE 1

Chemical composition of fly ash from the ECK power plant

Main components	Content [wt. %]	Trace components	Content [ppm]
SiO_2	47.31	Ba	1 452
Al_2O_3	25.19	Sr	699
Fe_2O_3	6.95	Y	56
MnO	0.08	Sc	27
MgO	2.88	Zr	128
CaO	3.84	Be	8
Na_2O	1.24	V	249
K_2O	2.65		
TiO_2	1.01		
P_2O_5	0.48		
LOI	7.26		
Σ =	98.89		

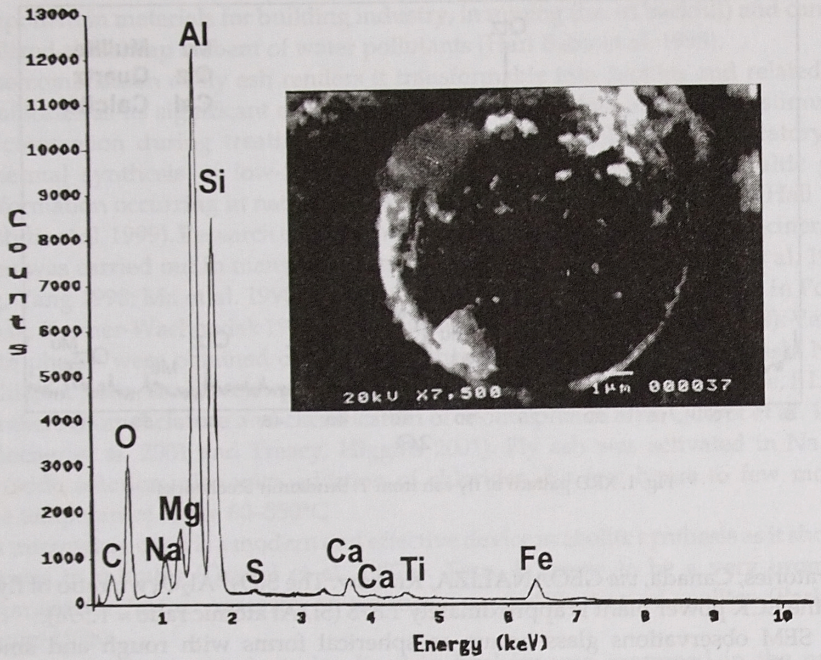

Fig. 2. SEM photo and EDS spectrum of aluminosilicate glass from the ECK power plant

Fig. 3. SEM image of metallic iron oxides particles from electrostatic precipitators of the ECK power

Experiments

Grounded samples of homogenous fly ash were treated in NaOH solution (with or without NaCl) in different conditions. The volume of solutions used in the experiments varied from 15 ml to 30 ml, and their concentration from 0.5M to 5M of NaOH and from 0 to 5M of NaCl. The mass of samples was 500 mg (Table 2).

The experiments were carried out using two types of microwave ovens.

➢ Samples of fly ash from the T. Sendzimir Steelworks were activated in a Milestone MLS-1200 microwave oven, in a closed system autoclave with PTFE vessels of 100-ml capacity. The vessels were not equipped with temperature or pressure

TABLE 2

Microwave oven assisted synthesis

Sample	NaOH v[ml]	NaOH c[mol]	NaCl v[ml]	NaCl c[mol]	Procedure	Products
H 5*	30	1	0	—	5min/250W + 25min/500W	H/Sod, Anc, Mu, Qtz
H 6*	15	1	15	1	5min/250W + 25min/500W	Sod, Mu, Qtz, Anc
H 13*	30	5	0	—	(5min/250W + 10min/500W + 10min/650W)·2	H/Sod, Qtz
H 17*	15	5	15	1	(5min/250W + 10min/500W + 10min/650W)·2	Sod, Qtz
H 18*	30	1	0	—	(5min/250W + 10min/500W + 10min/650W)·2	H/Sod, Qtz
E 43**	10	5	20	1	5min/60% + 10min/100%	Sod, Mu, Qtz
E 44**	10	5	20	1	10min/30% + 30min/60%	Sod, (Mu, Qtz)
E 45**	10	3	20	5	10min/30% + 30min/60%	Sod, (Mu, Qtz)
E 46**	10	3	20	5	10min/50% + 30min/80%	Sod
E 63**	30	0.5	0	—	10min/50% + 30min/80%	Mu, Qtz
E 64**	30	0.75	0	—	10min/50% + 30min/80%	Mu, Qtz, (H/Sod)
E 65**	30	1	0	—	10min/50% + 30min/80%	Mu, Qtz, H/Sod
E 72**	5	5	10	1	10min/60% + 40min/80%	Sod, Mu, Qtz
E 73**	5	5	10	1	10min/60% + 30min/100%	Sod, Mu, NaP1, Qtz
E 74**	5	1	15	1	10min/60% + 30min/100%	NaP1, Mu, Qtz
E 75**	5	1	20	3	10min/60% + 40min/100%	NaP1, Mu, Qtz

Sod — sodalite; H/Sod — hydroxysodalite; Anc — analcime; Mu — mullite; Qtz — quartz; NaP1 — synthetic zeolite of GIS structure; the content of phases in products — in order from higher to lower; phases in brackets — trace amounts.

H — samples from the T. Sendzimir Steelworks; E — samples from the ECK power plant.

* Milestone MLS-1200 microwave oven activation;

** UniClever microwave oven activation.

v — volume of solution used in reaction; c — concentration of solution used in reaction;

% — percent of maximum power of the UniClever microwave oven.

control instruments. Only energy of microwaves (W) and time of reaction (particular steps) could be pre-selected. Intensity of heating during reaction depended on the value of power set.

Two procedures were applied as following:

Procedure No 1

Step 1 — power 250 W, for 5 min
Step 2 — power 500 W, for 25 min
Cooling — 10 min

Procedure No 2

Step 1 — power 250 W, for 5 min
Step 2 — power 500 W, for 10 min
Step 3 — power 650 W, for 10 min
Cooling — 10 min

} repeated after 1 hour

➢ A UniClever microwave oven with a closed system autoclave was used for samples from the ECK power plant. A continuous measurement of temperature and pressure allowed to control the reaction conditions at any time. The conditions of procedures were described as: minimum and maximum pressure arrangement (in the range 24–27 atm or 25–28 atm), time, and power (in % of maximum). Syntheses were carried out in two steps, generally for 5 or 10 min at low power, then 10, 30 or 40 min at higher one (see Table 2).

After reactions all samples were filtered to remove supernatant liquid, washed with distilled water and dried.

Mineral products of the syntheses were identified by X-ray diffraction (XRD) using a Philips diffractometer with Philips X'pert software and the ClayLab program. The materials obtained were observed in a JEOL scanning electron microscope (SEM) and analysed by X-ray energy dispersive spectrometry (EDS).

RESULTS AND DISCUSSION

Several zeolite phases were synthesised (Table 2): sodalite and hydroxysodalite, NaP1, analcime (identification based on XRD patterns and nomenclature after Querol et al. 1997a).

Identified zeolite products include:

➢ sodalite — synthesised as a product of reactions at the quickest growth of temperatures or high concentration of NaOH and addition of NaCl in solution;
➢ hydroxysodalite — synthesised in similar conditions to sodalite, without using NaCl;
➢ NaP1 — synthesised during reaction with low-concentrated solutions or at low energy;
➢ analcime — a phase co-existing with sodalite and hydroxysodalite

From XRD patterns it appears that hydroxysodalite and sodalite were produced directly from initial material during synthesis at high energy, i.e. at a rapid growth of temperature and pressure (Fig. 4 and 5). If temperature increases slowly, without leaps

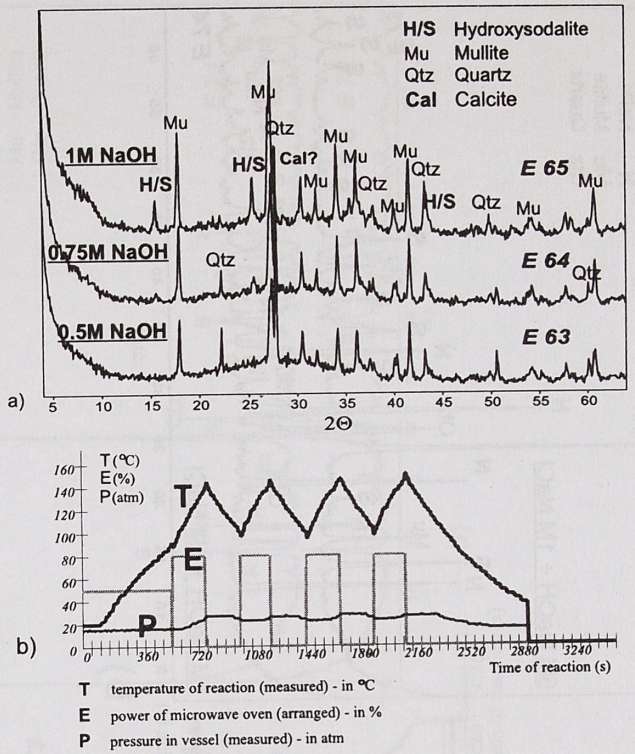

Fig. 4. XRD patterns of samples E63, E64, E65 (a) and conditiond of their reactions (b). Direct crystalization of hydroxysodalite from fly ash took place at higher concentrations of NaOH

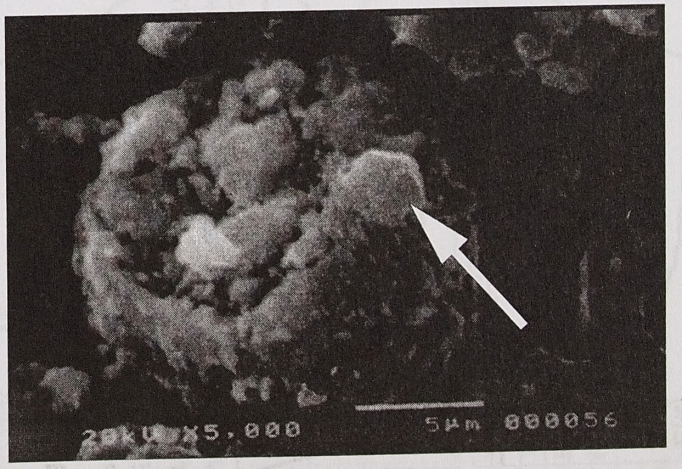

Fig. 5. SEM photo of sodalite crystal (arrow) growing on a glassy spherule

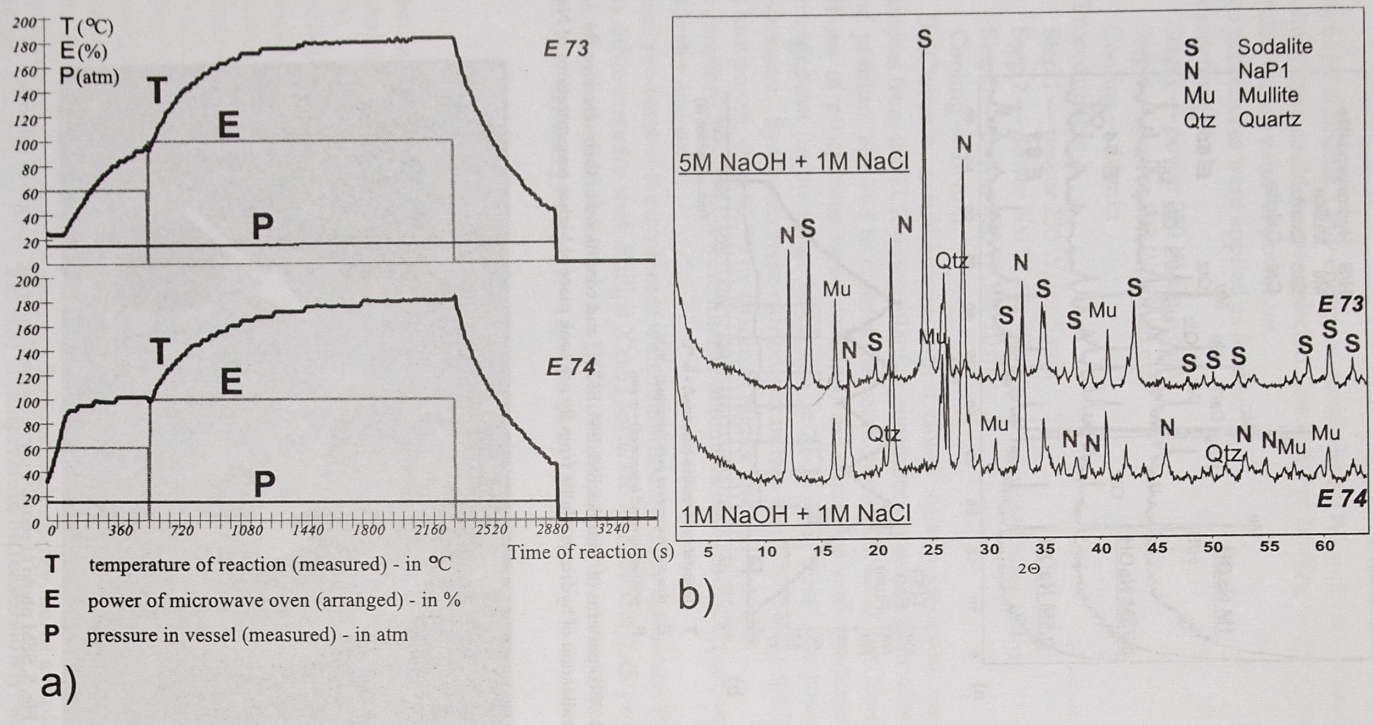

Fig. 6. Reactions with slow growth of temperature and different concentrations of NaOH
a — conditions of the reations; b — XRD patterns of the products (samples E73 and E74, see table 2)

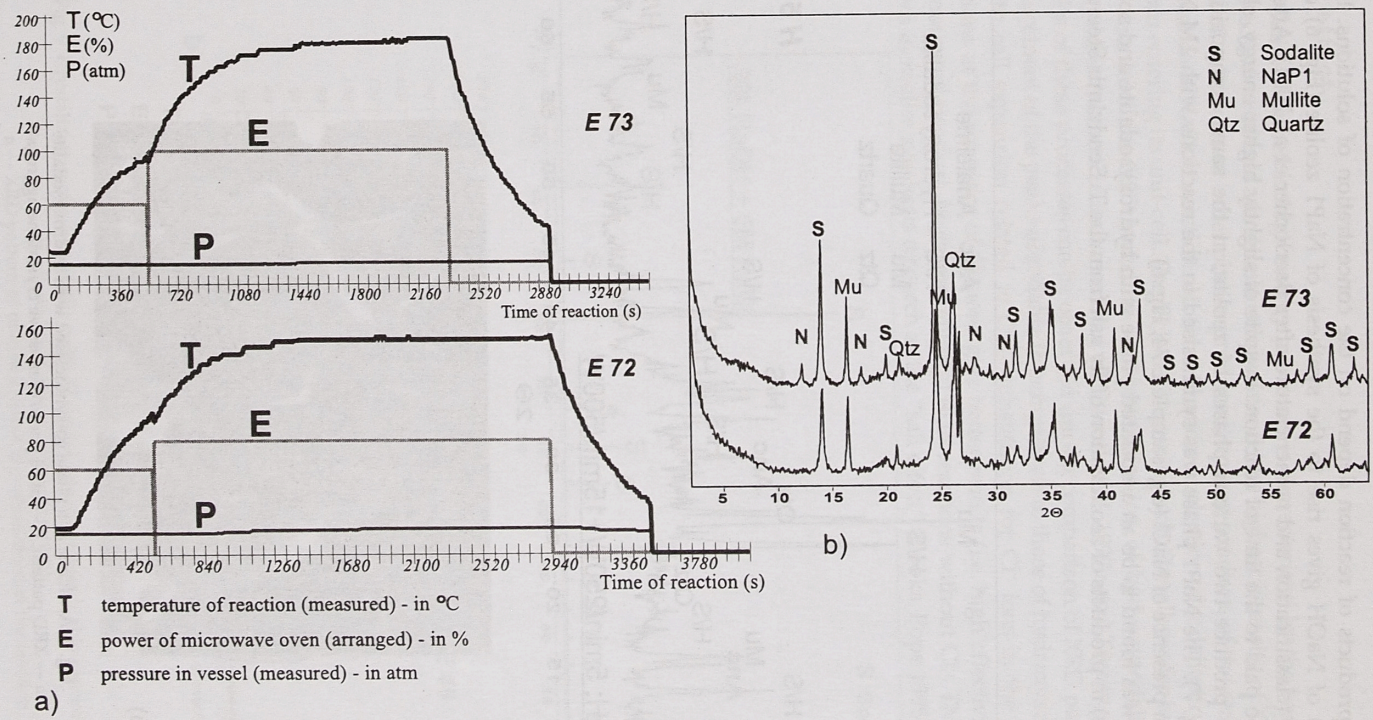

Fig. 7. Differences in mineral compositions of products of reactions at the same reagents (5 ml of 5M NaOH + 10 ml of 1M NaCl) and slightly different parameters of time and power
a — conditions of the reactions (various time and power); b — XRD patterns of received zeolites

of pressure, products of reaction depend on the concentration of solutions. Lower concentration of NaOH gives rise to the synthesis of NaP1 zeolite (Fig. 6) of the GIS structure (classification and nomenclature after Baerlocher et al. 2001). Attention should also be paid to the time of reaction. In spite of slightly higher energy, shorter reaction may produce two various phases of zeolite, at the same composition of solutions (Fig. 7). The NaP1 phase was synthesised in the reactions with 1M NaOH solution and a presence of NaCl (e.g. sample E 74, Fig. 6).

Analcime was found to be an associated phase with hydroxysodalite and sodalite (low amounts) in products of zeolitization of fly ash from the T. Sendzimir Steelworks (Fig. 8).

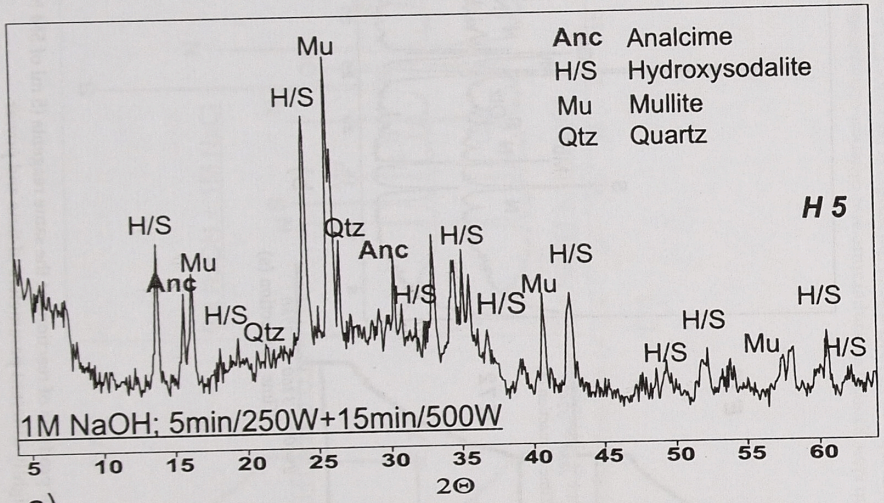

Fig. 8. Analcime as a phase co-synthesised with hydroxysodalite
a — XRD pattern; b — SEM photo of massive crystalline aggregate

Salt effect

Sodalite obtained in high energy processes is characterized by the best crystallinity, and the final products are almost monomineral (the highest intensity of XRD peaks and a lack of substrates or other phases produced) among products of the reactions (Fig. 9). A presence of NaCl in reaction solution enhances nucleation of sodalite crystals, with the Cl^- ions entering its unit-cell. The lack of Cl^- in initial solution allows for incorporation of OH^- ions into the SOD structure and crystallization of hydroxysodalite — sodalite octahydrate (nomenclature according to Querol et al. 1997a and Treacy, Higgins 2001). Results of these processes can be observed during comparison of XRD patterns as small displacement of the peaks of sodalite in comparison to those of hydroxysodalite (Fig. 10) due to cell expansion related to OH^- substitution for Cl^- ions in the structure. The reactions at the presence of Cl^- ions give better results (i.e. high effectivity of reaction, monomineral product, high crystallinity) than reactions without Cl^-. This regularity is known in zeolite synthesis research as the "salt effect" (Cooks, Pope 1995).

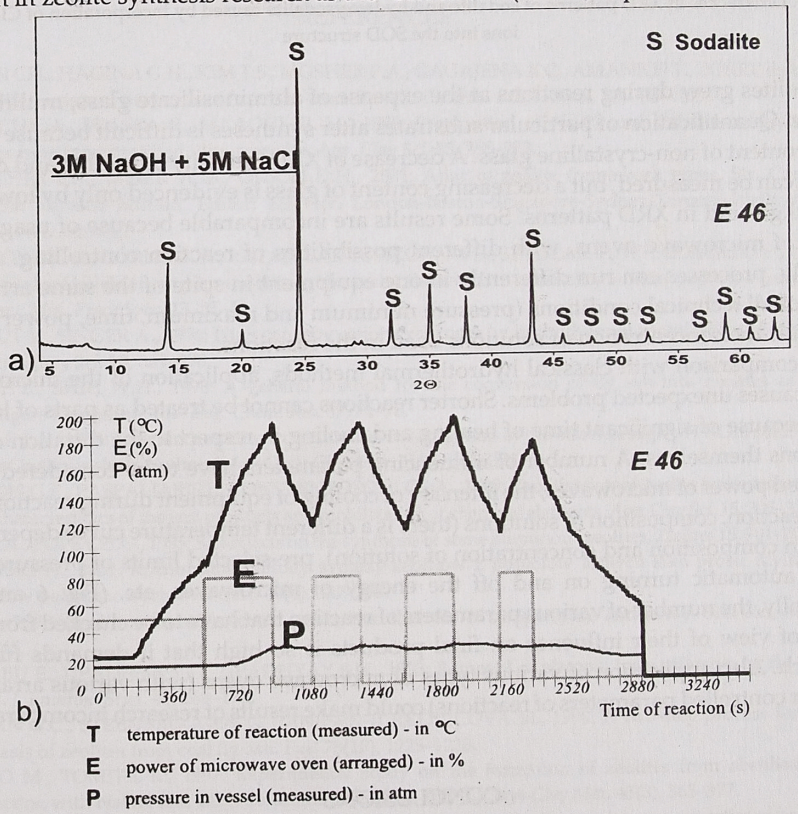

Fig. 9. Crystalization of pure sodalite (with Cl ions in structure) from highly concentrated solution (with rapid growth of temperature)
a — XRD pattern of obtained phase; b — conditions of the reaction

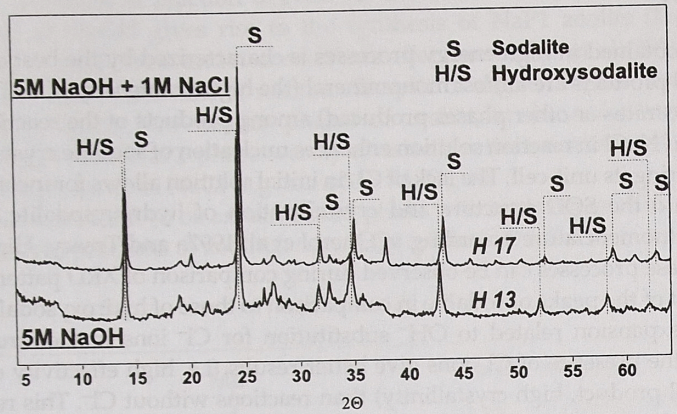

Fig. 10. Differences in XRD patterns of sodalite and hydroxysodalite caused by incorporation of Cl or OH ions into the SOD structure

Zeolites grew during reactions at the expense of aluminosilicate glass, mullite and quartz. Quantification of particular substrates after syntheses is difficult because of the high content of non-crystalline glass. A decrease of XRD intensity of mullite and quartz peaks can be measured, but a decreasing content of glass is evidenced only by lowering of background in XRD patterns. Some results are incomparable because of usage two types of microwave ovens, with different possibilities of reaction controlling. Additionally, processes can run differently in one equipment in spite of the same arrangement of all technical conditions (pressure minimum and maximum, time, power). The reason is the concentration of solutions used in the reactions.

In comparison with classical hydrothermal methods, application of the microwave oven causes unexpected problems. Shorter reactions cannot be treated as parts of longer runs because of significant time of heating and cooling in respect to the duration of the reactions themselves. A number of influencing parameters have to be considered: pre--selected power of microwaves, the intensity of cooling of equipment during reaction and after reaction, composition of solutions (there is a different temperature curve depending only on composition and concentration of solution), pre-selected limits of pressure that cause automatic turning on and off the energy of microwaves, etc. (Fig. 6 and 7). Generally, the number of various parameters of reaction that have to be checked from the point of view of their influence on final products is so high that it demands further research. Also application of various types of microwave ovens (with various arranged and/or controlled parameters of reactions) could make results of research incomparable.

CONCLUSIONS

1. The microwave oven is a useful equipment in zeolite synthesis. Its main advantage is shortening of the time of synthesis to minutes.

2. Fly ash from the ECK power plant and the T. Sendzimir Steelworks may be transformed into a zeolite-bearing material using microwave energy. Sodalite, hydroxysodalite and NaP1 zeolite phases were obtained during 25–50 min of reaction.

3. Syntheses carried out in the presence of NaCl are characterized by much higher zeolite productivity than similar ones without Cl^- ions. This is a reason that the products containing sodalite with Cl^- in its structure are monomineral and more crystalline than those containing hydroxysodalite with OH^- in its structure. Conditions of productivity of NaP1 are restricted to low concentration of NaOH solution and a slow increase of temperature and pressure during reaction.

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ZASTOSOWANIE PIECA MIKROFALOWEGO W SYNTEZIE ZEOLITÓW SODOWYCH Z POPIOŁÓW LOTNYCH (WYNIKI WSTĘPNE)

Streszczenie

Popioły lotne — najdrobniejsza frakcja odpadów paleniskowych — mogą być przetwarzane w zeolity ze względu na dużą zawartość Si i Al. Z elektrowni krakowskich pobrano próbki popiołów i poddano reakcjom z udziałem roztworów NaOH i NaCl o różnych stężeniach, przy użyciu pieców mikrofalowych Milestone MLS-1200 i UniClever. W wyniku reakcji w różnych warunkach otrzymano następujące fazy zeolitowe: sodalit, hydroksysodalit, NaP1 (faza typu GIS) i analcym. Najwyższą produktywność faz zeolitowych zaobserwowano podczas reakcji z udziałem jonów Cl^- w roztworze i przy wysokich (3–5 M) stężeniach NaOH. Zastosowanie pieca mikrofalowego w syntezie zeolitów wydatnie skraca czas syntezy do kilkudziesięciu minut, lecz rezultaty reakcji są o wiele trudniejsze do przewidzenia niż w klasycznej syntezie hydrotermalnej.